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LIGNAN AND NEOLIGNAN GLYCOSIDES FROM STEMS OF *ALANGIUM PREMNIFOLIUM*

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Key Word Index—*Alangium premnifolium*; Alangiaceae; stems; lignans; lignan glycoside; neolignan glycoside; alangilignosides A–D.

Abstract—From a methanol extract of stems of *Alangium premnifolium*, eight lignan derivatives were isolated. Structural elucidation by a spectroscopic method revealed that four of them were new lignan or neolignan glycosides. ©1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

From the leaves of *Alangium premnifolium* more than 15 megastigmane glycosides have been isolated [1–3]. Our continued interest in the chemistry of the stem of this species has led to the isolation of eight lignan and lignan glycosides. The present communication describes the isolation and structural elucidation of these glycosides.

RESULTS AND DISCUSSION

Chromatographic separation of a butanol soluble fraction of a methanol extract afforded eight lignan and lignan glycosides. Four were identified as the known compounds, lyoniresinol (**1a** and **1b**) [4], (+) and (−)-lyoniresinol 3a-*O*-*β*-D-glucopyranosides (**2** and **3**) [5, 6], and (+)-isolariciresinol 3a-*O*-*β*-D-glucopyranosides (**4**) [6], respectively, from spectroscopic analyses. From its optical rotation value ($[1\alpha]_D$+ 14.4°), lyoniresinol was expected to have been isolated as a mixture of enantiomers [4].

Alangilignoside A (**5**), $[\alpha]_D$+23.4°, was obtained as an amorphous powder, whose elemental composition was determined to be $C_{33}H_{46}O_{17}$ by observation of a quasi-molecular ion peak at *m/z* 549 in the negative ion HR-FAB mass spectrum. The IR spectrum indicated the presence of a hydroxyl group (3400 cm^{-1}) and benzene rings (1610 and 1500 cm^{-1}). The presence of a terminal xylopyranose and a 6-substituted glucopyranose was indicated by the ^{13}C NMR spectrum (Table 1). The remaining ^{13}C NMR signals consisted of those of two aromatic rings, one of which must have a symmetrical substitution, three methylenes, two of which are each expected to have an electronegative substituent from their chemical shifts (δ_C 66.1 and 71.5), and three methines, along with four methoxyl signals. From this evidence, **5** was assigned as a derivative of an aryl tetraline-type lignan glycoside. As found on comparison of the ^{13}C NMR chemical shift values with those of (+) and (−)-lyoniresinol 3a-*O*-*β*-D-glucopyranosides (**2** and **3**, respectively), the three spectra well coincided with each other. Although the differences between **2** and **5** were less than those between **3** and **5**, the maximum difference was 0.6 ppm at the C-2 positions of **3** and **5**. However, the CD spectra of these compounds clearly demonstrated that the aglycone of **5** is (+)-lyoniresinol (**1a**) [6]. Therefore, the structure of alangilignoside A was elucidated to be 6″-*β*-D-xylopyranosyl (+)-lyoniresinol 3a-*O*-*β*-D-glucopyranoside **5**, as shown in the formulae.

Alangilignoside B (**6**), $[\alpha]_D$−15.2°, was obtained as colourless needles. The elemental composition deduced by HR-FAB mass spectrometry was $C_{27}H_{34}O_{12}$ and the UV spectrum indicated that it had aromatic moieties. The ^{13}C NMR and ^1H NMR spectra showed the presence of symmetrically and asymmetrically tetrasubstituted benzene rings, a *trans*-double bond [δ_H 6.22 (*td*, J = 6 and 16 Hz) and 6.54 (*br d*, J = 16 Hz)], two primary alcohols, two characteristic signals (δ_C 88.9 with δ_H 5.59 and 55.5, with a proton

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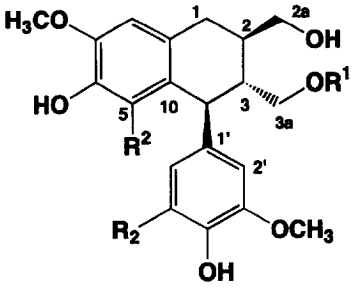
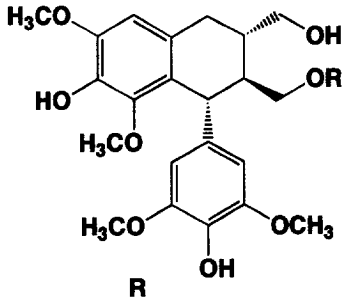
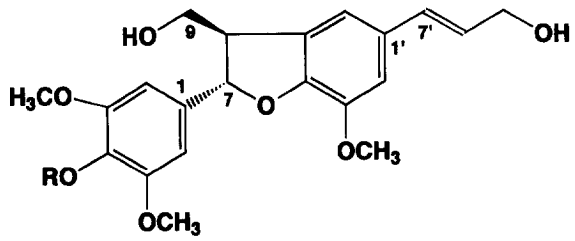


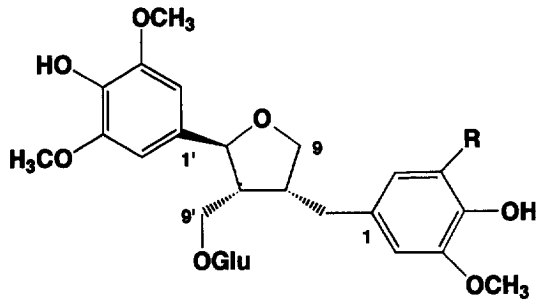
	R^1	R^2
1a	H	OCH_3
2	Glu	OCH_3
4	Glu	H
5	Glu(6)Xyl	OCH_3



	R
1b	H
3	Glu



	R
6	Glu
6a	H



	R
7	OCH_3
8	H

resonating at around δ_H 3.45) for a benzofuran type neolignan, and six signals for a β-glucopyranoside. Three methoxy signals, two of which were equivalent, were also observed in the NMR spectra. Therefore, a planar structure of the aglycone portion (**6a**) was suggested. Of the three hydroxyl groups which could form a glycosidic linkage, the phenolic one was concluded to participate, since, in the ^{13}C NMR spectrum, two primary alcohol carbons resonated at relatively high frequencies [δ_C 65.1 (C-9) and 63.9 (C-9′)], when compared with those reported for glucosides on hydroxyl groups in similar circumstances [7, 8]. This conclusion was further supported by a NOESY experiment, in which the methoxyl protons at the 3- and 5-positions (δ_H 3.82) crossed peaks with the anomeric proton (δ_H 4.87). The absolute configurations on the furan ring were determined to be 7-*S* and 8-*R*, respectively, from the observation of a negative Cotton effect at 272 nm ($\Delta\varepsilon - 5.84$) in the CD spectrum [9].

Alangilignoside C (**7**), $[\alpha]_D + 16.2°$, was obtained as colourless needles, whose elemental composition was determined to be $C_{27}H_{38}O_{13}$. The IR and UV spectra indicated the presence of aromatic rings and the ^{13}C NMR spectrum showed the presence of a β-glucopyranosyl moiety, two tetrasubstituted symmetrical benzene rings, three methylenes, two of which have oxygen functions, and three methine groups, one of which has an oxygen substituent, along with four methoxy signals [δ_H 3.82 (6H) and 3.83 (6H)]. From these functionalities, the aglycone was expected to be a tetrahydrofuranoid-type lignan; the ^{13}C NMR chemical shift values were essentially indistinguishable from those of the lignan xyloside, prupaside, obtained from *Prunus padus*, except for those of the sugar portion [10]. Enzymatic hydrolysis of **7** gave an aglycone whose sign of optical rotation value was the same as that of prupaside. Therefore, the structure of alangilignoside C was determined to be (8*R*, 7′*S*, 8′*R*)-5,5′-dimethoxylariciresinol 9′-*O*-β-D-glucopyranoside, as shown in formula **7**.

Alangilignoside D (**8**), $[\alpha]_D + 10.3°$, was obtained as an amorphous powder. The elemental composition deduced by negative ion HR-FAB mass spectrometry indicated that the M_r of **8** was 31 mu less than that of **7**. The ^{13}C and ^1H NMR spectra showed that it was also a tetrahydrofuranoid-type lignan, similar to alangilignoside C. The ABX-type coupling of three aromatic protons in the ^1H NMR spectrum was due to the loss of one methoxyl group from one of the benzene rings. In the difference NOE experiments, on irradiation of the protons at δ_H 2.75 (H-8) and 2.93 (H-7b), the signal intensities of both protons at δ_H 6.65 (*d*, J = 2 and 8 Hz) and 6.80 (*dd*, J = 2 Hz) were enhanced significantly, whereas on irradiation of δ_H 4.87 (H-7′), the proton at δ_H 6.65 (*s*) was enhanced. Therefore, the structure of alangilignoside D was determined to be 5-methoxylariciresinol 9′-*O*-β-D-glucopyranoside. The similar negative Cotton effects observed for alangilignosides C[$\Delta\varepsilon - 1.14$ (244)] and D[$\Delta\varepsilon - 0.73$ (239)] in the CD spectra indicated that the absolute stereochemistry of the tetrahydrofuran ring was the same as that of **7**, namely 8*R*, 7′*S* and 8′*R*.

Table 1. ^{13}C NMR data for alangilignosides A–D (**5**–**8**) (CD_3OD, 100 MHz)

Carbon no.	5	6	7	7a	8
1	34.0	135.0	136.0	136.0	135.0
2	40.6	104.5	107.1	107.0	113.5
2a	66.1				
3	46.7	154.5	149.3	149.3	149.0
3a	71.5				
4	43.1	140.1	134.9	134.9	145.8
5	148.7	154.5	149.3	149.3	116.2
6	138.9	104.5	107.1	107.0	122.3
7	147.7	88.9	34.5	34.2	33.9
8	107.9	55.5	44.0	43.9	43.9
9	130.2	65.1	73.7	73.6	73.6
10	126.5				
1′	139.5	132.9	133.0	132.9	133.7
2′	107.0	112.3	104.4	104.3	104.4
3′	149.5	145.6	149.3	149.3	149.2
4′	134.5	149.2	134.9	135.1	135.0
5′	149.0	130.0	149.3	149.3	149.2
6′	107.0	116.6	104.4	104.3	104.4
7′		131.9	84.4	84.2	84.5
8′		127.8	51.9	54.2	51.7
9′		63.9	68.0	60.6	68.6
1″	104.8	105.3	104.8		104.7
2″	75.1	75.8	75.3		75.2
3″	78.2	78.4	78.2		78.2
4″	71.6	71.4	71.7		71.7
5″	77.1	77.9	78.1		78.1
6″	69.9	62.6	62.8		62.8
1‴	105.6				
2‴	74.9				
3‴	77.7				
4‴	71.2				
5‴	66.9				
$-OCH_3$	60.2 on C-5	57.1 on C-3	56.9	56.8	56.5 on C-3
$-OCH_3$	56.7 on C-7	57.1 on C-5	56.9	56.8	56.9 on C-3′
$-OCH_3$	57.0 on C-3′	56.9 on C-3′	56.9	56.8	56.9 on C-5′
$-OCH_3$	57.0 on C-5′		56.9	56.8	

EXPERIMENTAL

General. Mps: uncorr. ^1H and ^{13}C NMR: 400 MHz and 100 MHz, respectively. Highly porous synthetic resin: Diaion HP-20 (Φ = 60 mm, L = 60 cm, frs of 1 l being collected). Reverse-phase gravity CC (RPCC) was performed with Cosmosil 75 ODS_{18}-OPN (Nakarai Tesque, Kyoto) (Φ = 40 mm, L = 25 cm, frs of 10 g being collected). The droplet counter-current chromatograph (DCCC) was equipped with 500 columns (Φ = 2 mm, L = 40 cm). The ascending method was used with $CHCl_3$–MeOH–H_2O–*n*-PrOH (9:12:8:2); and 5 g frs were collected and numbered according to elution with the mobile phase. Prep. HPLC: Inertsil (GL Science, Tokyo) (Φ = 20 mm, L = 250 mm), H_2O–MeOH, with flow rate and detection wavelength, 6 ml min^{-1} and 254 nm, respectively.

Plant material and isolation procedure. A. premnifolium Ohwi was collected on Okinawa island in 1990. The plant was identified by A.T. and a voucher specimen (AP-90-Okinawa) is deposited in the Herbarium of the Institute of Pharmaceutical Sciences of Hiroshima University School of Medicine. Dried and powdered stems (12.83 kg) were extracted with MeOH (45 l × 3) at *ca* 20°. The MeOH extract was concd to 1.5 l and, after the addition of 75 ml of H_2O, extracted with 1.5 l of *n*-hexane (44.7 g). The MeOH layer was evapd to a black mass, which was suspended in 1.5 l of H_2O and extracted with 1.5 l of EtOAc (49.6 g) and then with *n*-BuOH (1.5 l × 2) (106 g).

The residue (105 g) of the *n*-BuOH layer was subjected to Diaion HP-20 CC with 20% (8 l), 40% (12 l), 60% (12 l) and 80% (14 l) MeOH in H_2O. The residue (8.46 g, frs 13–15) of the 40% MeOH eluate was subjected to silica gel CC [400 g, $CHCl_3$ (2 l), and $CHCl_3$–MeOH (99:1, 3 l), (49:1, 6 l), (24:1, 3 l), (47:3, 6 l), (23:2, 9 l), (9:1, 9 l), (22:3, 6 l), (17:3, 6 l), (4:1, 3 l) and (3:1, 3 l), frs of 500 ml being collected]. The residue (2.3 g) of the 8–10% MeOH eluate (2.33 g, frs 45–60) was sepd by RPCC [MeOH–H_2O (1:9, 1 l) → (1:1, 1 l)]. The residue (827 mg) of frs 131–143 (1.72 g) was further sepd by DCCC into two frs, 38–48 (102 mg) and 49–60 (620 mg). The former fr. was finally purified by prep. HPLC [H_2O–MeOH (7:3), 42 min] to yield 49 mg of **4**. The latter fr. (102 mg) was also purified by prep. HPLC [H_2O–MeOH (7:3), 31 min and 35 min] to give 42 mg of **2** and 36 mg of **3**, respectively. The residue (1.04 g) of the 12–15% MeOH eluate on silica gel CC was sepd by RPCC [H_2O–MeOH (9:1, 1 l) → (1:1, 1 l), 390 mg, frs 150–156], DCCC (314 mg, frs 29–39) and then prep. HPLC [H_2O–MeOH (7:3), 34 min], which gave 73 mg of alangilignoside A (**5**).

The residue (30.7 g, frs 16–22) of the 60% MeOH eluate on Diaion HP-20 CC was subjected to silica gel CC [600 g, $CHCl_3$ (2 l), and $CHCl_3$-MeOH (99:1, 4 l), (49:1, 4 l), (24:1, 6 l), (47:3, 8 l), (23:2, 10 l), (9:1, 8 l), (22:3, 6 l), (17:3, 4 l) and (4:1, 2 l), frs of 500 ml being collected]. The residue (658 mg) of the 4–6% MeOH eluate of frs 22–31 was sepd by RPCC [H_2O–MeOH (9:1, 1 l) → (3:7, 1 l), 138 mg, frs 102–111], and then DCCC to give 101 mg of **1** in frs 156–180. The residue (2.03 g) of the 8% MeOH eluate (3.49 g, frs 44–45) was sepd by RPCC [H_2O–MeOH (9:1, 1 l) → (3:7, 1 l)]. The residue (670 mg) of frs 114–124 was sepd by DCCC to give two frs, 131 mg in 81–92 and 154 mg in 93–114. Final purification of the former fr. by prep. HPLC [H_2O–MeOH (3:2), 22 min] afforded 96 mg of alangilignoside D (**8**). Colourless needles (69 mg) of alangilignoside C (**7**) were obtained from the latter fr. The residue (2.02 g) of the 8–10% MeOH eluate (3.64 g, frs 55–70) was sepd by RPCC [H_2O–MeOH (9:1, 1 l) → (3:7, 1 l), 223 mg, frs 120–122] and then DCCC to give 44 mg in frs 81–94 and 70 mg in frs 95–110. From the former fr, 9 mg of alangilignoside B (**6**) was obtained by prep. HPLC [H_2O–MeOH (13:7), 24 min]. A further amount (23 mg) of alangilignoside C was re-crystallized from the latter fr.

Known compounds isolated. Lyoniresinol (**1**), $[\alpha]_D^{21}$ +14.4° (MeOH, *c* 0.83) [4]. (+)-Lyoniresinol-3a-*O*-β-D-glucopyranoside (**2**), $[\alpha]_D^{15}$ +47.0° (MeOH, *c* 0.81) [5]. (−)-Lyoniresinol-3a-*O*-β-D-glucopyranoside (**3**), $[\alpha]_D^{15}$ −53.6° (MeOH, *c* 0.80) [6]. (+)-Isolariciresinol-3a-*O*-β-D-glucopyranoside (**4**), $[\alpha]_D^{15}$ + 44.6° (MeOH, *c* 0.92) [6].

Alangilignoside A (**5**). Amorphous powder. $[\alpha]_D^{21}$ +23.4° (MeOH, *c* 0.92). IR ν_{max}^{KBr} cm^{-1}: 3400, 2900, 1610, 1500, 1460, 1420, 1320, 1215, 1115, 1040. UV λ_{max}^{MeOH} nm (log ε): 209 (4.75), 238 (4.08), 276 (3.55). ^1H NMR (CD_3OD): δ1.71 (1H, *m*, H-2), 2.06 (1H, *m*, H-3), 2.64 (1H, *dd*, *J* = 11 and 15 Hz, H-1a), 2.72 (1H, *dd*, *J* = 5 and 15 Hz, H-1b), 3.16 (1H, *dd*, *J* = 10 and 11 Hz, H-5‴a), 3.18 (1H, *dd*, *J* = 8 and 9 Hz, H-2‴), 3.24 (1H, *dd*, *J* = 8 and 9 Hz, H-2″), 3.29 (1H, *t*, *J* = 9 Hz, H-3‴), 3.33 (3H, *s*, −OCH_3 on C-5), 3.40 (1H, *ddd*, *J* = 2, 6 and 9 Hz, H-5″), 3.43 ~ 3.50 (2H, *m*, H-3aa and 4‴), 3.60 (1H, *dd*, *J* = 6 and 11 Hz, H-2aa), 3.67 (1H, *dd*, *J* = 4 and 11 Hz, H-2ab), 3.69 (1H, *dd*, *J* = 6 and 12 Hz, H-6″a), 3.74 (6H, *s*, −OCH_3 × 2 on C-3′ and 5′), 3.83 (1H, *dd*, *J* = 5 and 11 Hz, H-5‴*b*), 3.85 (3H, *s*, −OCH_3 on C-7), 3.92 (1H, *dd*, *J* = 5 and 10 Hz, H-3ab), 4.07 (1H, *dd*, *J* = 2 and 12 Hz, H-6″b), 4.24 (1H, *d*, *J* = 8 Hz, H-1″), 4.29 (1H, *d*, *J* = 8 Hz, H-1‴), 4.36 (1H, *d*, *J* = 7 Hz, H-4), 6.43 (2H, *s*, H_2-2′ and 6′), 6.57 (1H, *s*, H-8). ^{13}C NMR (CD_3OD): Table 1. CD (MeOH, *c* 0.00179) Δε (λ nm): −16.8 (217), +10.2 (244), +2.96 (273), −1.18 (288). HR-FAB-MS (negative centroid) *m/z*: 713. 2642 $[M-H]^-$ ($C_{33}H_{45}O_{17}$ requires 713.2657).

Alangilignoside B (**6**). Colourless needles, mp 116–118°. $[\alpha]_D^{20}$ −15.2° (MeOH, *c* 0.26). UV λ_{max}^{MeOH} nm (log ε): 208 (4.64), 224 (4.44), 273 (4.15). ^1H NMR (CD_3OD): δ3.19 (1H, *ddd*, *J* = 2, 5 and 10 Hz, H-5″), 3.38–3.52 (4H, *m*, H-8, 2″, 3″ and 4″), 3.64 (1H, *dd*, *J* = 5 and 12 Hz, H-6″a), 3.76 (1H, *dd*, *J* = 2 and 12 Hz, H-6″b), 3.79 (1H, *dd*, *J* = 4 and 11 Hz, H-9a), 3.87 (1H, *dd*, *J* = 5 and 11 Hz, H-9b), 3.82 (6H, *s*, −OCH_3 × 2 on C-3 and 5), 3.89 (3H, *s*, −OCH_3 on C-3′), 4.19 (2H, *dd*, *J* = 2 and 6 Hz, H_2-9′), 4.87 (1H, *d*, *J* = 8 Hz, H-1″), 5.59 (1H, *d*, *J* = 6 Hz, H-7), 6.22 (1H, *td*, *J* = 6 and 16 Hz, H-8′), 6.54 (1H, *br d*, *J* = 16 Hz, H-7′), 6.73 (2H, *s*, H_2-2 and 6), 6.95 (2H, *br s*, H_2-2′ and 6′). ^{13}C NMR (CD_3OD): Table 1. CD (MeOH, *c* 0.00132) Δε (λ nm): −4.12 (217), +7.92 (235), −5.85 (272), −4.74 (283). HR-FAB-MS (negative centroid) *m/z*: 549.1965 $[M-H]^-$ ($C_{27}H_{33}O_{12}$ requires 549.1972).

Alangilignoside C (**7**). Colourless needles, mp 168–170° (MeOH). $[\alpha]_D^{24}$ +16.2° (MeOH, *c* 0.74). IR ν_{max}^{KBr} cm^{-1}: 3300, 2900, 1610, 1515, 1460, 1430, 1385, 1365, 1325, 1305, 1280, 1230, 1165, 1110, 1075, 1040, 980, 955, 925, 890, 850, 835, 805. UV λ_{max}^{MeOH} nm (logε): 209 (4.80), 234 (4.12), 273 (3.45); ^1H NMR (CD_3OD): δ 2.51 (1H, *m*, H-8′), 2.52 (1H, *dd*, *J* = 7 and 13 Hz, H-7a), 2.77 (1H, *br sept*, *J* = 6 Hz, H-8), 2.96 (1H, *dd*, *J* = 5 and 13 Hz, H-7b), 3.22 (1H, *t*, *J* = 9 Hz, H-2″), 3.36 (1H, *t*, *J* = 9 Hz, H-4″), 3.67 (1H, *dd*, *J* = 5 and 12 Hz, H-6″a), 3.74–3.89 (3H, overlapped by envelopes of methoxyl signals, H_3-9a, 9′a and 6″b), 3.84 and 3.82 (each 6H, each *s*, −OCH_3 × 4), 4.01 (1H, *dd*, *J* = 7 and 8 Hz, H-9b), 4.08 (1H, *dd*, *J* = 6 and 10 Hz, H-9′b), 4.31 (1H, *d*, *J* = 8 Hz, H-1″), 4.86 (1H, *d*, *J* = 7 Hz, H-7′), 6.51 (2H, *s*, H_2-2 and 6), 6.65 (2H, *s*, H_2-2′ and 6′). ^{13}C NMR (CD_3OD): Table 1. CD (MeOH, *c* 0.00148) Δε (λ nm): +11.1 (211), −1.14 (244). HR-FAB-MS (negative centroid) *m/z*: 581.2244 $[M-H]^-$ ($C_{28}H_{37}O_{13}$ requires 581.2234).

Alangilignoside D (**8**). Amorphous powder. $[\alpha]_D^{24}$ +10.3° (MeOH, *c* 0.87). IR ν_{max}^{KBr} cm^{-1}: 3350, 2900,

1610, 1515, 1460, 1430, 1365, 1325, 1270, 1215, 1155, 1030, 900, 800. UV λ_{max}^{MeOH} nm (logε): 207 (4.69), 228 (4.14), 281 (3.61). ^{1}H NMR (CD_3OD): δ2.49 (1H, *qui*, J = 7 Hz, H-8′), 2.51 (1H, *dd*, J = 11 and 13 Hz, H-7a), 2.75 (1H, *qd*, J = 6 and 11 Hz, H-8), 2.93 (1H, *dd*, J = 5 and 13 Hz, H-7b), 3.23 (1H, *dd*, J = 8 and 9 Hz, H-2″), 3.37 (1H, *t*, J = 9 Hz, H-4″), 3.67 (1H, *dd*, J = 5 and 12 Hz, H-6″a), 3.75 (1H, *dd*, J = 6 and 8 Hz, H-9a), 3.77 (1H, *dd*, J = 7 and 10 Hz, H-9′a), 3.83 (6H, *s*, $-OCH_3 \times 2$ on C-3′ and 5′), 3.82 (3H, *s*, $-OCH_3$ on C-3), 3.87 (1H, *dd*, J = 2 and 12 Hz, H-6″b), 4.00 (1H, *dd*, J = 6 and 8 Hz, H-9b), 4.07 (1H, *dd*, J = 7 and 10 Hz, H-9′b), 4.30 (1H, *d*, J = 8 Hz, H-1″), 4.87 (1H, *d*, J = 6 Hz, H-7′), 6.65 (1H, *dd*, J = 2 and 8 Hz, H-6), 6.65 (2H, *s*, H-2′ and 6′), 6.71 (1H, *d*, J = 8 Hz, H-3′), 6.80 (1H, *d*, J = 2 Hz, H-2′). ^{13}C NMR (CD_3OD): Table 1. CD (MeOH, *c* 0.00174) $\Delta\varepsilon$ (λ nm): +7.13 (208), −0.73 (239). HR-FAB-MS (negative centroid) *m/z*: 551.2129 $[M-H]^-$ ($C_{27}H_{35}O_{12}$ requires 551.2128).

Enzymatic hydrolysis of alangilignoside C (**7**). Alangilignoside (24 mg) and crude hesperidinase (21 mg) were incubated at 37° for 2 hr in 2 ml of H_2O–DMSO (9:1). The hydrolyzate was subjected to silica gel CC [Φ = 18 mm, L = 200 mm, $CHCl_3$ (100 ml), $CHCl_3$–MeOH (19:1, 100 ml; 9:1, 100 ml; 7:3, 300 ml), frs of 12 ml being collected] to give 11.7 mg (67%) of (8*R*, 7′*S*, 8′*R*)-5,5′-dimethoxylariciresinol (**7a**) in frs 16–21 and 5.8 mg of D-glucose in frs 37–43.

(8R, 7′S, 8′R)-5,5′-*Dimethoxylariciresinol*. Colourless fine needles, mp 122–124° (MeOH). $[\alpha]_D^{19}$ +18.0° (MeOH, *c* 0.78). ^{1}H NMR (CD_3OD): δ2.38 (1H, *qui*, J = 7 Hz, H-8′), 2.49 (1H, *dd*, J = 11 and 13 Hz, H-7a), 2.74 (1H, *br sept*, J = 6 Hz, H-8), 2.93 (1H, *dd*, J = 5 and 13 Hz, H-7b), 3.66 (1H, *dd*, J = 7 and 11 Hz, H-9′a), 3.74 (1H, *dd*, J = 6 and 8 Hz, H-9a), 3.82 and 3.83 (each 6H, each *s*, $-OCH_3 \times 6$), 3.85 (1H, *dd*, J = 7 and 11 Hz, H-9′b), 4.00 (1H, *dd*, J = 6 and 8 Hz, H-9b), 4.76 (1H, *d*, J = 7 Hz, H-7′), 6.50 and 6.62 (each 2H, each *s*, H-2, 6, 2′ and 6′). ^{13}C NMR (CD_3OD): Table 1. HR-FAB-MS (negative centroid) *m/z*: 419.1741 $[M-H]^-$ ($C_{22}H_{27}O_8$ requires 419.1706). D-Glucose, $[\alpha]_D^{20}$ +33.3° (H_2O, *c* 0.39, after 24 hr being dissolved in H_2O).

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